

OST TECHNICAL PROGRESS REPORT FOR FY 1998

TITLE: CLEAN WATER TEAM

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DESCRIPTION: During FY 1998, the Water Pollution Team conducted basic and applied research related to the prediction, prevention, and treatment of water contaminated by the mining and processing of coal and metals. The team also developed and evaluated inexpensive water treatment technologies for inactive and abandoned sites that are currently the problems of local, State and Federal agencies.

RESEARCH OBJECTIVES: A primary objective of the Clean Water Team research efforts during FY 1998 was to develop and evaluate active, passive and biological treatment systems. Another major objective of the Team was to apply several non-intrusive geophysical techniques for site characterization and post-remediation evaluation of abandoned mine sites with environmental (water-related) problems.

LONG TERM GOALS/RELATIONSHIP TO FETC's PRODUCT LINE(S): The Clean Water Team conceives, plans, manages and conducts exploratory and applied research on water-related issues, especially those that relate to the extraction and utilization of coal. In addition, technical assistance is provided to various government agencies, industry, and public environmental groups. These activities support FETC's Watershed Science and Technology Initiative and FETC's efforts to provide regional leadership in this important area.

Mine drainage is one of the most wide-spread and visible sources of water pollution in the nation. Enormous loads of acid, metals and sulfates are deposited annually in the nation's streams and rivers as the result of uncontrolled and untreated mine drainage from abandoned and inactive coal and metal mines. The bulk of this pollution originates from underground mine pools, particularly in the eastern U.S. where rainfall is plentiful and the underground workings are relatively shallow and expansive in areal extent. FETC personnel, using relatively inexpensive and non-intrusive geophysical techniques, have developed techniques for identifying water loss zones in streams above underground mines. These same geophysical tools show potential for identifying the location of subsurface mine pools and water-filled fracture systems, which is significant in the cases where mine maps are inaccurate or non-existent and targeting of injection or monitoring wells is desired for remediation purposes.

Water treatment, and the related disposal of waste (sludge) generated from treatment, is very expensive. The active mining industry spends over a million dollars per day to treat mine

drainage. Passive treatment technology, which was pioneered by the Clean Water team personnel while part of the U. S. Bureau of Mines, is economical and is the primary abatement tool for government agencies and watershed organizations. Another alternative, which is currently being investigated by the Team, is the development of water-powered treatment systems and devices. The development of water-powered devices or treatment systems could reduce capital, operating and maintenance costs significantly and could potentially be constructed, operated and maintained by watershed organizations.

These investigations are addressing the following areas: (1) abandoned mine pool discharges which pollute rivers and streams, (2) low cost water treatment schemes coupled with the handling and disposal of the resultant waste product, (3) biological aspects of water pollution formation, remediation and resource recovery, and (4) non-intrusive geophysical applications for hydrological and post-remediation investigations.

SUMMARY OF ACCOMPLISHMENTS:

Acid mine drainage (AMD) from underground mines is a major environmental problem. The disposal of coal combustion by-products (CCB) is also a major national problem due to the large volumes produced annually and the economics associated with transportation and environmentally safe disposal. The concept of returning large volumes of the CCB to their point of origin, underground mines, and using the typically alkaline and pozzolanic attributes of the waste material for the remediation of AMD has been researched rather diligently during the past few years by various federal and state agencies and universities. As the result, the State of Maryland initiated a full-scale demonstration of this concept in a small, 5-acre, unmapped underground mine located near Friendsville, MD.

Through a cooperative agreement between the State of Maryland and the U.S. Department of Energy, several geophysical techniques were evaluated as potential tools for the post-injection evaluation of the underground mine site. Three non-intrusive geophysical surveys, two electromagnetic (EM) techniques and magnetometry, were conducted over the Frazee Mine, which is located on Winding Ridge near Friendsville, MD. The EM surveys were conducted to locate ground water in both mine void and overburden. The presence of magnetite, which is naturally inherent to CCB's due to the combustion process and essentially transparent in sedimentary rock, provided the reason for using magnetometry to locate the final resting place of the 100% CCB grout.

The data collected at this site indicate that a variety of non-intrusive geophysical techniques can be collectively used to conduct post-injection evaluations of remedial efforts (injections of CCB's). The terrain conductivity technique appeared to delineate the wet mine entries, which in the absence of mine maps, could be significant. The VLF technique appeared to locate water-filled fracture zones in the overburden, and also demonstrated the potential to locate existing or potential mine subsidence zones. The plotted gradiometer data, when not masked by the major anomalies produced by the steel cased wells, showed numerous and relatively subtle anomalies,

that may have been associated with the CCB injection.

RESULTS:

1. George: The objectives of the study were to characterize the occurrences of various metals and other components of coal mine drainage (CMD) and evaluate the relationships among water quality parameters by examining water quality analyses from 128 different discharges. The water quality analyses were of untreated drainage from active, reclaimed, and abandoned surface and underground mines, as well as coal waste materials. Most of the samples were obtained by the United States Bureau of Mines as part of its field sampling efforts, but some analyses from the mine drainage literature have also been incorporated. About 75% of the study sample set had pH values less than 4.5, with the remaining samples having pH values ranging from 4.5 to 6.9. The following metals were included in the chemical analyses: ferrous and ferric iron, aluminum, manganese, arsenic, beryllium, cadmium, cobalt, chromium, copper, antimony, and zinc. As would be expected by pH-controlled solubility relationships, higher metal concentrations were generally associated with lower pH values. Other general water quality parameters such as ionic strength and conductivity did not show as clear relationships with pH. Additionally, hardness was somewhat independent of pH over the range of the study sample set. This is significant since hardness usually raises the aquatic toxicity threshold for most metals (e.g., cadmium, chromium, copper, lead, manganese, nickel, and zinc). No clear correlations were found between the occurrence of manganese, which is a CMD treatment surrogate, with other more toxic metals. Potentially toxic concentrations of some of these metals were found at manganese concentrations less than 2 mg/L, which is the normal effluent standard for CMD discharges. A fairly good correlation was found between nickel and zinc concentrations. A strong correlation was found between conductivity and sulfate concentration. The components of acidity were also evaluated. While aluminum and both forms of iron dominated acidity below pH values of 4.5, ferrous iron was the major contributor toward acidity above pH 4.5. Manganese was a highly variable acidity contributor regardless of pH.

A study based on water quality analyses of 128 coal mine drainages has shown that toxic metals occur in these waters. Their occurrences in CMD display a striking similarity to some metal mine drainages. These metals can occur in concentrations that are significantly above aquatic life criteria as well as NPDES effluent standards. The study shows that the CMD water quality "spectrum" is quite wide. Despite this variation, metals and acidity show decreasing concentrations as pH increases. Despite the generally high hardness values for CMD, toxic metals can often exceed hardness-dependent aquatic life criteria. The high hardness values found in CMD may also inhibit the neutralizing effectiveness of limestone in passive treatment systems. The data indicate that AML reclamation efforts should include a full characterization of contaminated mine drainages prior to the development of treatment strategies. These efforts should move beyond the "traditional" CMD contaminants and also consider toxic metals and hardness in developing the remediation plan for an AML site.

Data base has been updated and analyzed. Several graphs have been generated looking for

occurrence of trace metals when manganese is below effluent limits, Also investigated the occurrence of trace metals at low levels of zinc and nickel to determine if either of these would serve as a better surrogate than manganese. Numerous correlation coefficients have been calculated to determine relationships between metals. A proposal to EPA to request funding to expand this project is being prepared.

2. George: Sampling of field sites was continued to build upon the data base already compiled (over 7 years of data) to document and evaluate the longevity and performance of various types of passive treatment systems. The treatment systems were selected because there is reliable, quantitative information available concerning their construction (we were involved in the design and construction of many of these sites). These sites contain all four of the major unit operations (aerobic wetlands, compost wetlands, anoxic limestone drains, and SAPS) and treat a wide range of water quality. Also, watershed groups and local and state agencies are involved in cleanup of these watersheds. Information concerning the performance of the passive treatment systems is furnished to these group as technical assistance. The following 12 systems have been monitored throughout the year: Howe Bridge # 1, Howe Bridge # 2, REM left ALD, REM right ALD, Filson # 5, Filson # 6, Jennings, Elklick, Oven Run site D, Oven Run site E, Schnepf, and Morrison. The water quality data has been analyzed and the results from several of these sites were included in a poster presentation at the 1998 Annual Meeting of the American Society for Surface Mining and Reclamation, May 17-22, 1998 in St Louis MO entitled "Seasonal and Long-Term Performance of Alkalinity-Producing Systems for the Treatment of Mine Drainage."

Monitoring at each site consisted of measuring flow, conducting field analyses (pH, temperature, conductivity, and alkalinity) and collecting water samples for complete laboratory analysis at several key locations to determine the performance of the various passive treatment unit operations. The performance of each system was examined for seasonal and long-term trends. In addition, these passive treatment systems were monitored for changes in metals other than iron and manganese that are not traditionally measured (i.e., Al, As, B, Ba, Cd, Co, Cu, Cr, Hg, Ni, Pb, Se, and Zn).

Letter reports outlining the performance of the Elklick I and the Oven Run Site D systems were prepared. The Elklick I report was sent the the MD Department of Environmental Resources. The Oven Run Site D report was sent to The USDA-NRCS, Congressman Murtha's office, and Damariscotta Environmental Consultants.

The Elklick I system has been very effective, treating over 17 million gallons of mine water. The following table reports the average influent and effluent water quality of fourteen separate sampling dates over the past three years.

Parameter	Influent	Effluent
pH, standard units	6.1*	7.1

Iron, mg/L	55.8	1.2
Manganese	5.1	2.3 [#]
Net Acidity/Net Alkalinity, mg/L as CaCO ₃	55.9 (net acid)	78.9 (net alkaline)
Flow, L/min	38.2	-

* without treatment, pH would naturally fall to ~2.9 due to precipitation of iron upon exposure to air.

manganese has averaged less than 1 mg/L over the past year.

Over the first three years of operation, this system has removed 7,700 lbs of iron and has generated over 19,000 lbs (~10 tons) of alkalinity as CaCO₃. The system shows no signs of any reduction in performance. At the rate of 3.3 tons of limestone dissolving per year, there is enough limestone in the system to theoretically last another 50 years.

The Oven Run Site D system has been very effective, treating over 116 million gallons of mine water, even though its design flow rate was often exceeded. The following table reports the average influent and effluent water quality of twelve separate sampling dates over the past two years.

Parameter	Influent*	Effluent*
pH, standard units	3.8	6.7
Iron, mg/L	34.6	0.39
Aluminum, mg/L	2.0	0.40
Net Acidity/Net Alkalinity, mg/L as CaCO ₃	177 (net acid)	22 (net alkaline)
Flow, L/min	407	426

* influent = discharge of pond #1, effluent = discharge of pond #3.

Over the first two years of operation, this system has removed 33,000 lbs of iron and 1,500 lbs of aluminum and has generated over 134,000 lbs (67 tons) of alkalinity as CaCO₃.

Columns Studies

Two columns have been operated in our laboratory over the past 3 years. The first column simulates a downward, vertical-flow anaerobic wetland, also referred to as successive alkalinity-producing systems (SAPS), and has received mine drainage for more than years. The 0.16-m diameter column is vertically oriented and (from bottom to top) consisted of a 0.30-m

thick layer of limestone, a 0.76-m thick layer of spent mushroom compost, and 0.91 m of free standing water. Water flows vertically downward through the system. A second column, filled with only limestone, receives water from the same source as the first column. This limestone column contains a 1.06-m thick layer of limestone and 0.91 m of free standing water and has received water for more than years. Actual acid mine drainage (pH = 3.1, acidity = 200 mg/L (as CaCO_3), SO_4^{2-} = 600 mg/L, Total Fe = 10 mg/L, Mn = 14 mg/L, and Al = 18 mg/L) was collected every two weeks from a nearby abandoned deep mine and applied to these columns at a rate of 3.8 mL/min. Sampling ports are positioned at various vertical positions within each column.

Data has been entered into a spreadsheet and analyzed. Results of columns have impacted current design of full-scale field systems to maximize sulfate reduction. The experimental design has been used by others in other laboratory SAPS simulations (University of Oviedo, Spain; University of Georgia/Savannah River Environmental Lab, Virginia Polytechnic University). Columns have recently been shut down for transport to another building.

Presentations and Publications

Abstract published and poster presented entitled “Seasonal and Long-term Performance of Alkalinity-Producing Passive Systems for the Treatment of Mine Drainage” by George R. Watzlaf at the 1998 American Society for Surface Mining and Reclamation meeting in St. Louis, Missouri, May 17-22, 1998.

Invited by the Planning Committee to International Scientific/Technical Meeting on Water in the Closure of Mines in Oviedo, Spain, March 23-25, 1998. Four papers were presented - “The Characterization of Mine Drainage for the Design of Passive Treatment Systems,” “The Utilization of Passive Treatment Systems for the Treatment of Acid Mine Drainage: Wetlands,” “The Utilization of Passive Treatment Systems for the Treatment of Acid Mine Drainage: Anoxic Limestone Drains,” “The Utilization of Passive Treatment Systems for the Treatment of Acid Mine Drainage: Mixed Systems.”

Invited to present “Passive Treatment and Watershed Organizations” at the Nineteenth Annual West Virginia Surface Mine Drainage Task Force Symposium in Morgantown, WV, April 7-8, 1998.

Final version of “Chapter 5 - Passive Systems Technology” for inclusion in the Acid Drainage Technology Initiative (ADTI) AMD manual entitled “Handbook of Technologies for the Avoidance and Remediation of Acid Mine Drainage” was completed and submitted.

Invited to present “Passive Treatment for Acid Mine Drainage Control” and serve on a round table discussion panel at the Fourth Annual Mine Drainage Conference and National Coalition for Abandoned Mine Reclamation Annual Meeting in Knoxville, TN, September 10-12, 1998.

Invited to present the results of field and lab studies in “Passive Treatment of AMD Remediation, Design and Construction of Wetlands and Anoxic Limestone Drains” at the Acid Mine Drainage Formation and Abatement Technology Conference in State College, PA, September 28- 30, 1998.

3. Terry/Karl: In-Line System - Shadle Discharge

Background: The ILS, which is a DOE patented treatment system and can be utilized as a water-powered device in scenarios with 50 feet or greater of elevation change or head. The ILS requires a minimum of 20 psi (approx. 50ft) of water pressure to operate. The topography and orientation (vertical) of the coalbeds in the anthracite region can provide this necessary criteria, such that mine water often discharges out of the mines at elevations significantly above the valley floor. The inactive Shadle Mine site offered an opportunity to demonstrate: (1) the ability of the ILS to treat a severely polluted water and (2) the potential application at numerous sites throughout the anthracite region that require aeration and/or alkaline addition. As stated above, previous tests were associated with mine waters (Rowe Tunnel and Tracy Airhole) that were circum-neutral in nature with low concentrations of metals. The Shadle Mine drainage is very acidic and contains high concentrations of metals, particularly iron.

The following ILS tests were completed without use of gravity-head, such that a pump was used with a small-scale (8 gal/min) system. This is a standard approach for identifying operating parameters for the system and determining accurate alkalinity requirements before installing a large-scale system. The treatment reagents used for these tests included conventional sodium hydroxide (NaOH) and acid mine drainage (AMD) treatment sludge, produced at the near-by Rauch Treatment Plant operated by the PA Department of Environmental Protection. The application of AMD sludge was an attempt to utilize the excess alkalinity typically associated with calcium hydroxide (lime) treatment and conventional processes. Two series of tests, one with NaOH and the other with lime sludge, were conducted. During these tests pH adjustments were made to cover a range of units (between approximately pH 5 and pH 9) with corresponding water samples being collected with each adjustment. Water samples were collected at the entrance (before the jet pump) and discharge of the system (after discharging from the static mixer). Raw water samples (without alkaline addition) were also collected (at the same locations) at the beginning and end of each test series. It should be noted that the discharged raw water samples were aerated by the system, although no alkaline reagents were added. Alkaline reagents were added to the system through the jet pump.

NaOH Treatment: A 50% NaOH solution was purchased for these tests and in order to be able to control the pH (by pumping solution into the jet pump with a peristaltic pump) it had to be diluted down to a 5 % solution. Table 1 shows the data collected for this test. Samples SH-1 and SH-10 represent the raw water quality entering the system. The acidity load ranged between approximately 750 and 850 mg/L. The subsequent samples, SH-2 and SH-11, illustrate that aeration of this water without alkaline addition has no effect on this acidic water quality, as expected. Samples SH-3 through SH-9 and SH-12 show the effects of a variety of pH

adjustments, that ranged between approximately pH 5 and pH 9. The best overall treatment, in terms of metals removal was at the adjustment pH 9.2 (SH-7). This sample, SH-7, shows essentially complete iron removal (relative to mining standards), excess alkalinity, and acceptable aluminum and manganese concentrations. It should be noted that the aluminum concentration was showing an increasing trend, as would be expected at this pH, and that a higher pH adjustment would likely result in higher concentrations and represent a threat to aquatic life. The next best water quality was shown in sample SH-8, which had a pH 8.65 and overall good metals removal that was similar to sample SH-7, however, the manganese concentration was slightly elevated at 5.4 mg/L. Other samples SH-4, SH-6, and SH-12 which are in the upper pH 7 range (pH 7.91, pH 7.75, and pH 7.95), show a net alkalinity, iron levels below 3 mg/L (typically good for mining requirements), acceptable aluminum concentrations; however again, all samples in this lower pH range have elevated manganese levels (11.3, 10.8 and 8.6 mg/L, respectively).

The ILS has demonstrated the ability to neutralize the acidic mine water, oxidize ferrous iron concentrations in the range of 374 to 380 mg/L to below 3 mg/L, and bring out other metals to within acceptable levels during the brief 30 second contact time of the system. Previous ILS tests have shown the ILS to be about 30% more efficient in terms of reagent (CaOH₂, CaO, and NaOH) use in conventional treatment processes. In the case of sample SH-7 (see table below), which appears to satisfy all treatment requirements, measured flow rates show that 101.1 gallons per day (or 36,901 gallons per year) of 5% NaOH solution would be required at this site. A 5-gallon can of technical grade 50% NaOH solution was used for testing and with dilution to a 5 % solution a cost of \$1.75 per gallon was calculated. Consequently, for sample SH-7 the cost of chemicals on a daily and yearly basis would be \$177 and \$64,577, respectively. It should be noted that these unit costs would be reduced if a lower grade solution was used and if the solution was purchased in bulk or in dry form and mixed on-site.

Table 1. ILS test data using NaOH as the alkaline reagent are shown in terms of mg/L.

Parameter	RAW WATER			RAW WATER									
	IN		OUT	IN									OUT
	SH-1	SH-2	SH-3	SH-4	SH-5	SH-6	SH-7	SH-8	SH-9	SH-10	SH-11	SH-12	
pH - lab	3.26	3.48	5.47	7.91	5.59	7.75	9.26	8.65	7.12	3.41	3.40	7.95	
pH - field	3.19	3.56	5.87	7.87	5.97	7.74	9.05	8.23	7.00	3.57	3.55	7.20	
Dis. oxy.	4.32	8.68	7.58	0.76	3.31	0.25	0.15	0.16	0.10	3.11	8.22	0.08	
Alkalinity	0	0	0	95.2	0	83	154	111	72.4	0	0	97.8	
Acidity	766	752	372	<10	323	<10	0	0	<10	843	837	<10	
Ferrous Iron	374	369	233	2.3	191	2.6	0	0	46.9	383	372	1.31	
Total Iron	374	369	233	2.3	191	2.6	0.05	0.37	46.9	383	372	1.31	
Calcium	163	160	158	151	160	150	134	147	158	164	159	149	
Aluminum	24.4	24.2	0.45	0.06	<0.04	0.1	0.36	0.13	0.33	24.75	24.1	0.1	
Manganese	24.7	24.5	23.9	11.3	24.5	10.8	0.73	5.4	16.7	25.5	24.8	8.6	

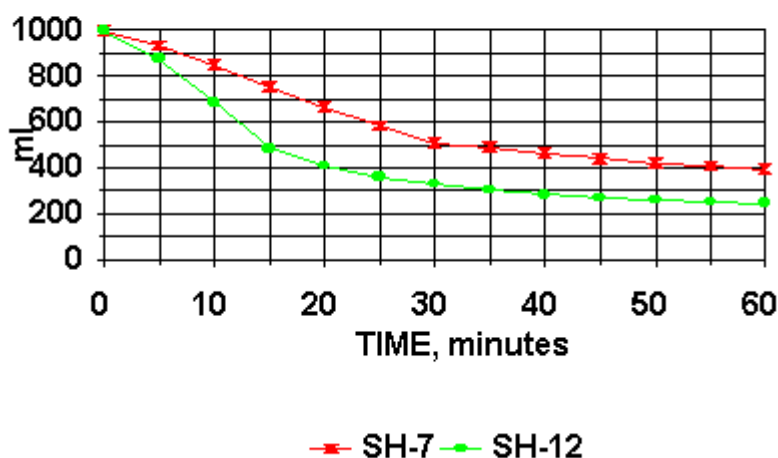
Sulfate 1717 1699 1626 1676 1648 1659 **1641** 1659 1689 1735 1687 1662

Reagent

Gal/day

NA NA 90.7

1-HOUR SLUDGE SETTLING 1,000 ml GRADUATED CYLINDER



	NA	NA	ND	ND	56.4	81.1	101.1	94.5	91.4	
Gal/year	NA	NA	ND	ND	20586	29601	36901	34492	33361	33105

Sodium Hydroxide Sludge: One-hour sludge settling tests, using samples SH-7 and SH-12, were conducted using a 1,000 ml (glass) graduated cylinder with readings being taken on five-minute intervals. Figure 1 shows a plot of the test data. These preliminary settling tests showed that a well defined sludge-water interface developed and settled to levels of 395 and 245 ml for SH-7 and SH-12, respectively. An extended reading taken for sample SH-12, approximately 22 hours later, was measured 135 ml. A 100 ml is equivalent to 1 7/16 inches, likewise, 50 ml is equivalent to 23/32 of an inch.

Figure 1. Graph of one-hour sludge settling tests for samples SH-7 and SH-12.

As was mentioned above, the zero point charges for amorphous $\text{Fe}(\text{OH})_3$ and alpha FeOOH are 8.5 and 7.8 respectively. The pH for sample SH-7 was about 9.3 whereas sample SH-12 had a pH of only 7.9. Again, it is reasonable to expect that electrostatic repulsion of the charged surfaces becomes large enough to interfere with agglomeration, at least for sample SH-7, only this time the pH value is too high. This suggests that there exists an optimum pH for effective iron removal. The pH must be high enough for the oxidation to proceed at a significant rate, but not so high that the surface of the solid becomes so strongly charged that it causes settling problems.

AMD Treatment Sludge: Fresh AMD sludge, generated at a local treatment plant, was tested as an alternative alkaline reagent since it would be free and readily available if effective. This exploratory attempt was targeted at using the excess lime in the sludge, that typically occurs as the result of inefficiencies in all conventional lime treatment operations. Furthermore, this approach was being pursued to do a preliminary evaluation of the sludge settling characteristics. The sludge was collected at the treatment facility and brought to the site in drums. This sludge was delivered to the jet pump using a 2 inch submersible pump that re-circulated the sludge (to prevent settling) in a drum and had a small split-line with a valve to control the delivery rate.

It was determined during these tests that regardless of the flow rate of sludge being delivered to the jet pump, the pH could not be driven above 7.5 (see table 2, field pH). Sample SHS-7, which had a field pH of 7.58, provided the best metals removal and was one of the highest pH's obtained. Note that sample SHS-5 had a lab pH of 8.0; however, the field pH was 6.77 and this discrepancy suggests a procedure error either in the field or lab in particular sample. Sample SHS-7 provided the best water quality improvement of all the sludge treatment tests. This approach worked well in terms of net alkalinity, reduced iron and aluminum (<2 and 0.22 mg/L, respectively); however, the manganese concentrations significantly increased from 25.03 up to 43.54 mg/L. Table 2 shows that manganese concentrations increased significantly in all treated samples, regardless of pH adjustment. It is apparent that existing manganese in the AMD treatment sludge (being used as the alkaline reagent) had resolubilized and resulted in an increase in manganese concentration in the ILS effluent water. This increase in manganese concentration could be the result of simple resolubilization of an oxide precipitated during the original DEP treatment that produced the sludge, or an ion exchange of protons for the metal cation on the sludge surface as the pH was reduced by contact with the Shadle water. Due primarily to this increase, rather than decrease in metal (manganese) loading, this source of readily available alkalinity will not be pursued.

Table 2. ILS test data using AMD sludge as the alkaline reagent are shown in terms of mg/L.

Parameter	RAW WATER								RAW WATER	
	IN	OUT							IN	OUT
	SHS-1	SHS-2	SHS-3	SHS-4	SHS-5	SHS-6	SHS-7	SHS-8	SHS-9	
pH - lab	3.41	3.39	4.65	7.35	8.00	6.30	7.98	3.42	3.41	
pH - field	3.61	3.55	5.00	7.45	6.77	6.39	7.58	3.51	3.46	
Dis. oxy.	4.57	9.01	8.83	0.33	0.91	0.37	0.72	3.21	8.53	
Alkalinity	0	0	0	37.9	39.2	16.8	74.6	0	0	
Acidity	874	835	626	<10	<10	80.8	<10	768	788	
Ferrous Iron	376	367	354	2.26	3.16	87.1	<1.1	372	369	
Total Iron	376	367	354	3.23	4.47	87.1	1.2	372	369	
Calcium	161	157	165	167	163	176	151	160	159	
Aluminum	24.27	23.83	6.57	0.14	0.17	0.08	0.22	24.05	23.86	
Manganese	25.03	24.49	41.73	90.49	42.96	106.94	43.54	25.06	24.6	

Sulfate 1705 1667 1624 1257 1157 1435 961 1881 1671

Finally, a synoptic sampling of Loriberry Creek was performed at locations above and below the point discharge (road culvert) where the Shadle Mine drainage enters the stream. Other Shadle Mine discharge points also exist at points further down-stream; however, influences of other drainage sources are involved and the impact can not be clearly related solely to the Shadle Mine. A review of Table 3 shows a slight, but overall degradation of water quality. Greatest impact on water quality is the aluminum concentration, which is increased by an order of magnitude.

Table 3. Synoptic sampling of Loriberry Creek above and below a point where the Shadle Mine discharge enters the stream.

	UP-STREAM	DOWN- STREAM	CULVERT
Parameter	LC3	LC4	LC1
pH - lab	5.25	4.90	3.24
pH - field	6.05	5.34	3.25
Dis. oxy.	8.81	8.63	6.20
Alkalinity	<2	<2	0
Acidity	<10	<10	178
Ferrous Iron	5.30	5.67	36.20
Total Iron	5.30	5.67	63.03
Calcium	14.12	14.87	75.64
Aluminum	0.04	0.25	11.85
Manganese	1.93	2.01	10.20
Sulfate	122	127	650

4. Rick: Water Treatment with Metal Recovery using Bacterial Sulfate Reduction

Bacterial sulfate reduction water treatment strategies have been developed by more than 10 years of research, including bench- and pilot-scale testing. The research is approaching maturity, and the technology is now ready for large-scale, field demonstrations and transfer to industry. Goals for FY98 were to facilitate the transfer of bacterial sulfate reduction treatment technology to industry, to validate recent advances in bioreactor design, and to explore niche applications for the technology.

In FY98, FETC contributed to the design of an EPA-sponsored, bacterial sulfate reduction treatment demonstration to be conducted by MSE at Berkeley Pit in FY99. This plan calls for a 10 gpm treatment plant that will recover copper and zinc concentrates to offset treatment costs. Other components of the Berkeley Pit water may also be recovered if markets can be identified. The first step towards commercialization of this technology is obtaining EPA acceptance. Our efforts at assuring a successful demonstration at Berkeley Pit is our best avenue for obtaining EPA's blessing.

FY98 research was primarily directed toward independent verification of sulfate reduction rates claimed by Paques, Inc. (our industry partner) for a new, hydrogen-fueled, gas-lift loop bioreactor. Their claimed sulfate reduction rates were 2.5 to 3 times faster than the best rates obtainable using currently available bioreactors. Because sulfate reduction is the rate-limiting step in water treatment, use of the new bioreactors could double or triple water treatment capacity with significant cost savings.

A pilot-scale, hydrogen-fueled, gas-lift loop bioreactor was assembled and operated at FETC during FY98. Although claimed sulfate reduction rates were eventually achieved in these tests, bioreactor startup was difficult and the operation was often inconsistent. Suspected causes of the erratic performance were systematically eliminated by trial and error. Bioreactor performance was eventually linked to the retention of metal sulfide sludge (to which the active biomass was attached) in the bioreactor. A more consistent performance was obtained by attaching a lamella clarifier to the bioreactor outflow, and recycling the clarifier underflow back to the bioreactor. This minimized biomass loss and allowed the bioreactor to achieve claimed sulfate reduction rates. Operational guidelines for the consistent, long-term performance of hydrogen-fueled, gas-lift loop bioreactors were partly developed by this research, although additional work is needed.

In FY97 and 98, bacterial sulfate reduction treatment was successfully applied to scrubber blowdown waters, possibly the greatest challenge for any water treatment technology. These waters are extremely acidic, and contain high concentrations of every RCRA toxic element except silver. Conventional forms of water treatment are incapable of treating scrubber blowdown waters, and the EPA's best available demonstrated technology can only treat moderately contaminated blowdown waters (albeit at great expense). The treatment results obtained at FETC has encouraged ASARCO, Inc. to partner with FETC and Paques, Inc. to sponsor additional research in this area.

5. Pete: Sludge Reduction
P.Hesbach

S.Lamey,

The sludges generated by the chemical processes used to remove metals from contaminated streams and seepages present a significant disposal problem, both due to the number of such treatments and the voluminous nature of the material. The low solids and high water content provide an opportunity for meaningful research to address the volume reduction need. Treatment of sludges from metals contamination sources with carbon dioxide has been suggested as a potential method to reduce these sludge volumes, and this treatment has been the focus of metal sludge research. Experiments were run using several mixtures of carbon dioxide in inert gas from 100% CO₂ to 15%, an amount that might be present in combustion exhaust.

The sludge types examined were from individual metals of concern, from mixtures of these metals, from mixtures modified to have concentrations similar to those found in the Omega mine drainage water, and from authentic Omega treatment inlet samples. The authentic samples were monitored for stability during storage to ensure their integrity during short series of experiments

in which treatment conditions were varied. Both the amounts of specific metals and the iron ferrous to ferric ratio can vary significantly in month-to-month sampling at the Omega site. The sludge was generated by the addition of hydrated lime or by the action of anhydrous ammonia, the latter being the method used at the Omega site. Other variables included the pH level at which the metals were removed and the pH of the water after CO₂ treatment. Treated sludges were monitored for settling rate and solids content. Settling rate relates to the water throughput rate in a field treatment scenario. The greater the solids content, the less water that is in the gel matrix, water that must be handled when the sludge is ultimately disposed. A smaller sludge volume allows for a smaller holding pond as sludge settles. Both sludges and their supernatants were analyzed for metals content.

Laboratory improvements were made to add gas delivery lines and flow controls, and the reaction vessel was fitted with an internal pH monitoring electrode. Sludges were run with controls that included agitation from an inert gas and an untreated sample. Typically, sludges from ammonia were less dense (less solids and more water) than from hydrated lime. For ferric iron, CO₂ provided greater sludge density and faster settling with lime sludges, but no advantage for ammonia generated sludges. For ferrous iron, the lime sludge was only slightly aided by CO₂, whereas the ammonia sludges were denser and settled faster if CO₂ was allowed to bring the pH down to 7.5. For aluminum, ammonia sludges were denser and settled faster if the pH was only brought down to 8.5 with CO₂, and ammonia produced denser, faster settling sludges than hydrated lime for this metal. Copper and zinc lime sludges were better without CO₂, but the gas aided zinc ammonia sludges. Copper produced no precipitate from ammonia. Manganese sludges settled faster and had greater density from both methods when treated with CO₂, although much of this was due to resolubilization when the pH dropped. For a number of metals, resolubilization under modified treatment conditions becomes significant. Resolubilization can be due to amphoteric behavior that produces soluble hydroxy species, or due to the formation of soluble ammonia complexes. These properties can manifest themselves in selected pH range windows for effective metals removal. Unfortunately, these windows do not all optimize at the same value. Significant work remains to be done to gain a more fundamental understanding of sludge matrix properties. Greater knowledge of their formation and destruction will allow for more effective treatments at specific mine drainage sites.

A research proposal was submitted to continue this work, with the inclusion of some basic science that will allow future treatments to be more effectively designed for the chemical species present in a given contaminated source. Another proposal was submitted that seeks to address a specific water contamination site on the National Priorities List.

In addition to the laboratory sludge work, project personnel have been working with the West Virginia Department of Environmental Protection (WVDEP) on various aspects of the remediation of the Omega Mine Complex. The intention of this project is to reduce the generation of acid mine drainage (AMD) from the mine. The portion of the project presently being conducted by the sludge group personnel involves sampling approximately 15 locations around the mine complex. These 15 sampling locations are discharging acid mine drainage in

quantities ranging from milliliters per minute to gallons per minute. AMD samples have been collected by sludge personnel at Morgantown since November 1997. The samples are then analyzed for total acidity and metal concentrations. In the spring of 1998, a grout mixture consisting of coal combustion fly ash, FBC ash, and cement was injected into the mine to attempt to reduce the generation of AMD. Samples collected before and after the grouting are being compared to determine the effect of the grouting on the quantity and composition of the AMD released. Sludge personnel have also been involved in the construction and placement of an in-line system (ILS), an apparatus for mixing a slurry with a liquid side stream, at the Omega complex. The ILS will be used to add mixtures of ash and cement to the AMD discharge at the treatment inlet site in order to assess possible ways to utilize these types of mixtures to reduce the volume of sludge produced at the site.

6. Hank: 1. Inhibition of Bacterial Acid Production in Underground Coal Mines.

Weekly to biweekly trips were taken underground in the Safety Research Coal Mine. Water samples for microbiological analysis were routinely taken at 7 sites that covered a pH range of approx. 3 to 7. Various solid and liquid growth media were evaluated. Specific progress was made on the use of techniques to identify fungi isolated from the underground coal mine. Numerous isolates were obtained, and the identification methods used were significantly different from routine bacteriological procedures. Numerous new media and isolation methods were tested. Fungi and/or fungal spores appear to be ubiquitous throughout the mine environment these were found to be extremely diverse, although dominated by *Penicillium* and *Gliocladium* spp. The ability of fungal spores to move easily throughout the mine environment, via natural air currents and mine ventilation, suggests that discoveries of unique metabolic capabilities within this group of organisms may be useful in the development of biological strategies for the inhibition of bacteria involved in the formation of acid mine drainage. One slightly acidic site was found to contain an unidentified flagellate protozoan.

Samples of coal from an exposed face in Room 13 and from several cm below the exposed surface were sampled aseptically and were incubated in liquid growth medium. This experiment indicated that microbial (bacterial and fungal) activity could be detected on the coal surface and within the coal seam using conventional culture methods.

Bacterial and fungal isolates with distinctive morphologies were selected and isolated via successive transfer to additional solid media. Of those cultures presumed to be bacteria based on colony appearance on solid media, one proved to be a fungus, possibly a yeast (similar to *Candida*). Of the remaining cultures, 40% were Gram positive and 60% were Gram negative. At least 40% of the Gram negative isolates were highly motile in liquid culture; none of Gram positive isolates were motile, and preliminary signs of spores (typically *Bacillus* spp.) were observed in some cells. Preliminary incubation of selected isolates on Biolog ID plates was carried out. The metabolic data obtained with these plates were used to establish a data base for environmental isolates obtained in the mine, and are also being used to confirm duplicate strains among those being studied.

The protocols for the preparation and inoculation of bacterial isolates using the Biolog ID test plates were tested and practiced. Bacterial strains growing in 6 liquid media after 4 weeks at room temperature were examined directly and plated on solid media. 9K medium for the enrichment of iron-oxidizing bacteria indicated iron oxidation after 1 week by a sample taken from an acid water sump in the mine, whereas iron oxidation occurred after 3 weeks when inoculated with a sample from a pH-neutral mine roof seep. Protein analysis of cells taken from the mine environment was done using the Bradford method, with cell lysis methods of alkaline hydrolysis, ultrasonic and physical disruption being tested. Contacts were made with Environmental Resources Management, who promised cooperation with the bacterial analysis and subsampling of drill core material from coal mine sites in PA and OH when needed.

Active cultures of *Thiobacillus* species (*T. thioparus*, *T. neapolitanus*, and *T. denitrificans*), as well as other pure cultures of bacteria, were grown and maintained on solid and liquid media. These will be used to carry out preliminary work on extraction, amplification and identification of genetic material, specifically 16S rRNA sequences and randomly amplified polymorphic DNA, via the polymerase chain reaction. Experiments were carried out to determine the possible role of neutrophilic (neutral pH) thiobacilli in the acidification of microenvironments, creating conditions suitable for the metabolism of *T. ferrooxidans* and other acidophilic iron-oxidizing bacteria.

In-situ experiments were carried out in the flooded underground mine at the Brinkerton - Sewickley Creek site. Microscope slides were suspended by fishing line into the mine void of the Pittsburgh seam in well #5 in the well field; these test slides were either plain glass or were coated with powdered pyrite attached with silicone rubber cement. Pyrite samples from the Iron Mountain Mine (California) and Elura Mine (Australia) sites were used. Slides were recovered after long-term incubation for evidence of microbial colonization and pyrite degradation. These data are currently being analyzed.

A novel monitoring device to ascertain geochemical conditions was also designed and deployed in well #5 so that it would remain suspended in the flooded mine. This device consisted of a 64-well microliter plate containing gel suspensions of a number of solid chemical compounds (e.g. manganese carbonate, ferric oxide, zinc sulfide, manganese dioxide, lead oxide, manganese sulfide, ferric sulfide). In addition, resazurin dye (redox indicator) and polyhydroxybutyrate were tested as possible geochemical/metabolic activity indicators. The device was recovered and analyzed after a 2 to 3 week incubation in the mine; results showed that the method was successful in the remote determination of the redox conditions in the flooded mine. Enough oxygen was found to be present to successfully oxidize all MnS present in the wells, but not oxidize FeS. The results were encouraging enough to suggest that future research could produce a geochemical sensing method analogous to the BIOLOG method used to speciate bacteria.

Several experiments quality control experiments were conducted to verify the efficiency of the BIOLOG bacterial ID system. Four known organisms, *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Staphylococcus epidermis* were chosen as the test

organisms. The organisms were grown on two different media, tryptic soy agar and nutrient agar, that are commonly used in the laboratory. Results indicate that the BIOLOG system was capable of repeatedly identifying both the *E. coli* and *P. aeruginosa*, but unable to identify either *Staphylococcus* species at any time. This result is possibly explained by the use of a different growth media than recommended. Results of this test indicated that both *E. coli* and *P. aeruginosa* were satisfactory control organisms when grown on either nutrient agar or tryptic soy agar. Additionally, because the BIOLOG system depends on the proper technique, tests were carried out comparing the results of different laboratory personnel on the same organisms. These tests showed no significant difference between results obtained by different researchers. Other variables tested were inoculum pH and iron concentration in the inoculum. To resolve these questions, a series of saline solutions, pH 1.0, 3.0, 5.0 and 6.4 were used as inocula for BIOLOG plates to determine if the acidic pH could result in false positives. Other plates were inoculated with an iron-containing medium to determine if the iron interfered with plate results. No false positives were observed in any of these experiments and the results indicated that acidic, iron-containing inoculum could be used with the BIOLOG system.

2. In-Situ Stabilization of Heavy Metals In Soil

Experiments were carried using heavy metal-amended soil to which various organic and biopolymeric materials, as well as gypsum, had been added previously to enhance bacterial sulfate reduction and stabilize heavy metals. Initial sequential extractions of soil had been carried out after 1 month of incubation. The second set of sequential extractions was done after 18 months total incubation, under less-stringent incubation conditions of humidity and anaerobiosis than the original experiment. Results showed that metals immobilized in soil via bacterial sulfate reduction activity during the initial time frame were partially remobilized after long-term exposure to oxidizing conditions and lack of moisture. These data were presented in May at the annual meeting of the American Society for Microbiology.

3. In-Situ Capping Of Metal-Contaminated Sediments.

Experiments were done in the Wilson Run sludge pond to further determine the nature of iron cycling in that environment. Three sediment cores were taken about 25 meters from shore. These cores were immediately sectioned in 1 cm intervals. Upon return to the lab, samples were centrifuged under argon gas, the supernatants were collected, filtered, acidified, and sent to the analytical lab for total dissolved iron analysis by ICP. At the time the cores were taken in the field, surficial iron hydroxide sediment in the pond was collected, added to molten agar solution, and poured into redox gel probes, which were allowed to harden. These probes, as well as control probes containing no sediment, were placed vertically in the sediment at the approximate location where the cores were taken. Replicate probes were immediately sliced into 1 cm sections and returned to the lab. There each slice was acid-digested and digests were sent to the analytical lab for total iron analysis. After two weeks incubation in place, the probes in the field

were collected, sliced immediately, and processed as described above. The purpose of the redox gel probe experiment was to determine in situ rates of iron oxyhydroxide sediment dissolution with depth in the sediment using actual surficial sediment material that will eventually be buried within the sediment column. Analysis of porewater iron profiles for the three cores showed that two of the cores had high concentrations of total dissolved iron (25 - 30 mg/L) near the surface of the sediment, while the third core had a relatively thick (3 cm) oxidized zone containing no dissolved iron. These data suggest that a net positive diffusive iron flux from the sediments to the water column occurs, and that biogeochemical processes in these sediments may vary widely on an areal basis.

Sediment cores were taken for the construction of an aquarium sediment system in the lab. The porewater equilibrator adjacent to the baffle was removed from sediment, and porewater samples were filtered and acidified. Double-sided gel probes containing MnO₂ and FeS were placed adjacent to the baffle. FeS-containing gel probes placed one month before were recovered from the sludge pond; preliminary analysis indicates that FeS oxidation occurred to greater depths in the sediment closer to the outlet of the sludge pond, but that this was not extensive (several cm at most). Virtually no oxidation of FeS was noted along the central transect (across the pond) below the sediment-water interface. These two observations suggest that the FeS oxidation observed in these sediments may be correlated with increased water flow along the sediment-water interface. It also appears that FeS probes placed in the Wilson Run system were only sensitive indicators of oxygen penetration and overall FeS stability, and do not serve as good indicators of zones of iron hydroxide reduction.

Nine different sediment capping materials (fly ashes, sand, soil, etc.) were placed in the Wilson Run sludge pond and were left in-situ for 3 months (June through September). After this time, redox gel probes containing MnO₂ and FeS were pushed into sediments within each cap and were left in place for one week. Two cores were then collected from each cap and control area (18 total cores). The sediments were extruded in the lab, sectioned every cm for 15 cm depth, centrifuged under argon atmosphere, and sent for analysis of porewater metal concentrations by ICP. Redox gel probes were sectioned and acid-digested for total metal content. Solid sediment from each core slice was acid-digested with aqua regia for total metal analysis. Data will be presented at a national meeting in November 1998.

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7. Terry: Geophysical techniques were used to assess the hydrologic conditions that pose serious environmental problems in mined lands of the United States. Mining and the presence of subsurface mine workings cause problems such as water pollution and the disruption of natural hydrologic flow. Geophysical techniques provide tools to determine bedrock and hydrologic conditions. This information can be used to identify the extent of the environmental problem, to monitor temporal changes in the subsurface conditions, and to plan remediation and determine its effectiveness. Case studies from three underground mine sites demonstrate the successful use of near-surface geophysics to address hydrologic problems.

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